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1.0 EXECUTIVE SUMMARY

The purpose of this Phase I, Small Business Innovative Research (SBIR) program was to find a non-destructive test technique which could be used to determine the loss in mechanical properties of an adhesive bond following environmental exposure. The non-destructive test technique utilized for this study was the dielectric relaxation spectroscopy (DRS) technique and the loss in mechanical properties was monitored using the double notch shear (DRS), adhesive bonded, joint test specimens.

The dielectric relaxation data revealed that although the relaxation times did increase with moisture content at a given test temperature, the relaxation times did not change with increasing moisture content. Calculations were then made for the dielectric relaxation strength. The dielectric relaxation strength also increased with moisture content; however, in this case increases in moisture content of the adhesive did result in additional increases in the relaxation strength.

The shear strengths of the bonded joint test specimens were then determined for both the dry condition and after environmental exposure. In this case, although the shear strength was reduced by moisture in the adhesive, increasing amounts of moisture did not generally result in further reductions in shear strength. However, for the three test specimens in which there was data available, there did appear to be a possible correlation between the dielectric relaxation strength, the moisture content and the ultimate shear strength of the adhesive.

2.0 INTRODUCTION

This nine-month, Phase I, Small Business Technology Transfer (STTR) program, entitled "Dielectric Relaxation Spectroscopy of Adhesively Bonded Joints", Contract No. F49620-98-C-0073 began 1 September 1998. The work was a joint effort between the Department of Chemical Engineering, Chemistry and Material Science, Polytechnic University, Brooklyn, NY and the small business firm, AdTech Systems Research, Inc, Dayton, OH. The aim of this program was to show the feasibility of developing a non-destructive evaluation (NDE) technique that could be correlated to the mechanical behavior of an adhesively bonded structure after exposure to a hygrothermal environment. The non-destructive evaluation techniques utilized for this program were Dielectric Relaxation Spectroscopy and Fourier Transform Infrared (FTIR) Spectroscopy. The mechanical behavior of the bonded joints was assessed using Double Notch Shear (DNS) specimens.

3.0 BACKGROUND

Adhesive bonding is often used in aircraft, automobile and other structural applications. It has always been a desirable method of joining two or more components since bonded joints generally have better strength to weight ratios than mechanically fastened joints. Bonded joints, however, are generally susceptible to the effects of moisture, which is usually the main factor behind strength degradation of the joint.

The effect of an aggressive environment on the adhesive is usually measured by changes in macroscopic properties, such as changes in mechanical shear strength. The loss in mechanical properties, however, is thought to be the result of numerous chemical/physical changes occurring in the adhesive at the microscopic level. This program will attempt to 1) understand the microscopic chemical/physical changes in the adhesive upon hygrothermal exposure, 2) correlate that information to changes in the mechanical properties.

The proposed work was divided into three phases. Phase I entails the identification of actual physical changes occurring in the adhesive after exposure to a hygrothermal environment; Phase II entails the development of a methodology for monitoring these changes; and Phase III entails the formulation of a model to correlate the physical changes to the changes in mechanical properties.

The first phase of the program, identification of the physical nature of the changes occurring, in the adhesive will be addressed using Fourier Transform Infrared (FTIR) Spectroscopy. This technique will be used to identify the exact chemical changes occurring in the adhesive as a result of exposure to an aggressive environment. Absorbed moisture is thought to affect the vibrational modes of the characteristic groups and moieties that participate in hydrogen bonding. FTIR was therefore being used to find evidence of hydrogen bonding between the absorbed water and the epoxy matrix. In particular, the interactions between polar groups and water molecules are of interest, since the epoxy-amine systems contains -OH groups after curing. The near infrared (NIR) region (4000 cm^{-1} to about 9000 cm^{-1}), where several peaks related to -OH groups are located, was determined to be the region of interest.

The second phase of the program entailed finding a technique to monitor these physical changes. Dielectric Relaxation Spectroscopy (DRS) was chosen because it provides extensive information about a host of chemical and physical phenomena occurring in adhesively bonded joints. Absorbed moisture is thought to migrate into the adhesive in the form of hydrogen bonding and cluster formation. This absorbed moisture alters the local environment of the adhesive. Changes in the local environment of the adhesive affects the dipole relaxation and reorientation dynamics in the adhesive, changes that are monitored by the dielectric relaxation technique. It was thought that even a small amount of absorbed moisture would alter the nature and speed of the molecular motions in the adhesive. Hence it was anticipated that even small amounts of absorbed moisture could be monitored using the dielectric relaxation technique. Although the dielectric phenomena monitored by this technique include interfacial polarization, interfacial reactions, charge migration and dipole reorientation, for this program, only the molecular motions associated with dipole relaxation and reorientation were monitored.

The third phase of the work entailed trying to find a model to correlate the actual physical changes in the adhesive to the changes in mechanical properties as a result of moisture intrusion. Changes in mechanical behavior resulting from moisture absorption include plasticization of the adhesive, lower shear strength, and eventual diffusion of moisture to the adhesive/adherend interface, resulting in adhesive versus cohesive failures. The dielectric relaxation technique was therefore chosen to find changes in the dipole relaxation measurements and to correlate these changes to changes in the mechanical properties of the adhesive as measured by ultimate shear strength.

4.0 OBJECTIVE

This program had two objectives. The first objective was to determine whether or not Dielectric Relaxation Spectroscopy (DRS), in conjunction with Fourier Transform Infrared Spectroscopy, could be used as a viable NDE technique to evaluate the pre-damage state of adhesively bonded joints exposed to an aggressive hygrothermal environment. The second objective was to correlate the DRS observations with changes in the mechanical property data obtained from double notch shear specimens exposed to various moisture saturation levels.

5.0 TEST PROGRAM AND TEST MATRICES

The Phase I test program was broken down into five tasks. Task 1 was the selection of materials and the fabrication of the bonded joint test specimens; Task 2 was the environmental exposure and mechanical testing of the bonded joints; Task 3 was the analysis of the bonded joint test specimens; Task 4 was the non-destructive evaluation of the bonded joint test specimens; and Task 5 was data correlation between the dielectric relaxation and the mechanical test results in the final technical report. The schedule for the Phase I tasks is shown in Figure 1. AdTech performed Tasks 1, 2, 3 and 5 while Task 4 was performed by Brooklyn Polytechnic University.

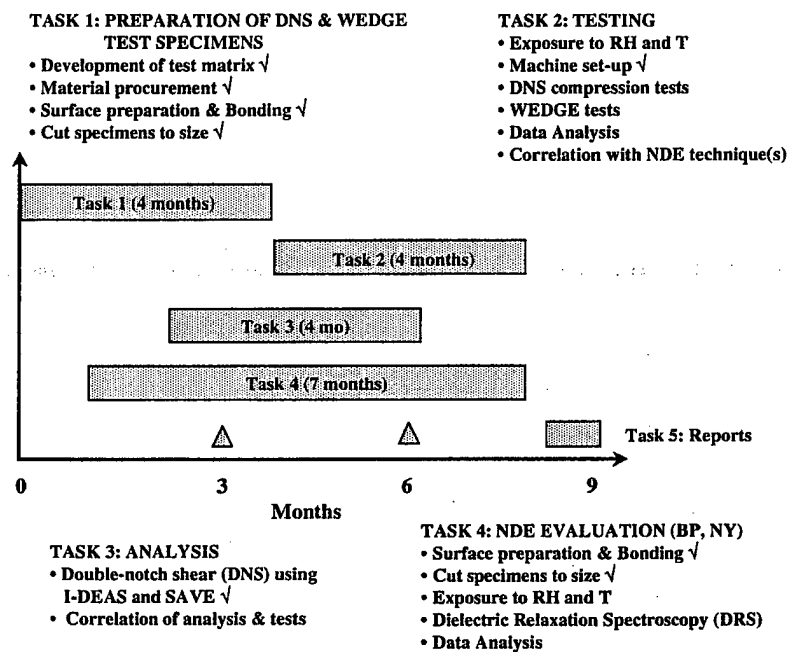


Figure 1. Schedule for the Phase I tasks

5.1 Test Matrix for the Dielectric Relaxation Spectroscopy Program

The matrix for the Dielectric Relaxation Spectroscopy testing is shown in Table 1. Following cure, some specimens were designated dry and immediately tested with DRS. Others were

placed into the controlled humidity chambers for different times, temperatures, humidity conditions to infuse moisture into the specimens. These specimens were designated "humidity-aged" and were tested at various temperatures using the DRS technique.

Initial work was conducted on extreme test conditions. Tests were first conducted on dry specimens, those with no humidity aging, and then on specimens after 15 hours exposure at room temperature and 50% relative humidity, and then on specimens exposed for 720 hours at room temperature and 98% relative humidity. Finally, one test was conducted after 90 hours of moisture exposure at 70°C and 98% relative humidity. Additional testing was later conducted on specimens after 72, 120, and 240 hours exposure at 60°C and 98% relative humidity.

Table 1. Test matrix for the Dielectric Spectroscopy Program

| Time ↓ | Temp ⇒ | 24°C | 60°C | 70°C |
|------------|---------|------|------|------|
| Humidity ↓ | | | | |
| None | | x | | |
| 50% RH | 15 hrs | x | | |
| 98% RH | 720 hrs | x | | |
| 98% RH | 90 hrs | | | x |
| 98% RH | 72 hrs | | x | |
| 98 % RH | 120 hrs | | x | |
| 98% RH | 240 hrs | | x | |

5.2 Test Matrix for the Mechanical Testing Program

The test matrix for the double notch shear specimens is identified in Table 2. The purpose of this particular test matrix was to create different levels of moisture saturation in the specimens and then to try to correlate the amount of moisture in the adhesive to specific losses in mechanical properties.

Specimens were first tested at room temperature (RT) without any aggressive environmental exposure. These specimens were used to determine the baseline, ultimate shear strength of the adhesive. One set of specimens was then subjected to a 24 hour boiling water test to determine the worst case condition for humidity aging. Following this, six sets of test specimens were exposed to different relative humidity levels (62% and 98%) at each of three different temperature conditions (room temperature, 60°C and 82°C) for 184-hour exposure periods. Finally, two more test groups were tested at 60°C, at both 62% and 98% relative humidity for 312 hours exposure.

Table 2. Test matrix for the double notch shear specimens

| Temp ⇒ | Room Temp | 60 °C | 82 °C | 60 °C | 100 °C |
|------------------|--------------|---------|---------|---------|--------|
| Humidity ⇓ | | | | | |
| 15 % | s-4 | | | | |
| 62 % | s-15 | s-12 | s-11 | s-10 | |
| 98 % | s-9 | s-16 | s-14 | s-13 | |
| Boiling Water | | | | | s-7 |
| Exposure Time | 184 hrs | 184 hrs | 184 hrs | 312 hrs | 24 hrs |

6.0 SPECIMEN PREPARATION AND FABRICATION

For Task 1 of this study, 2024-T3 base aluminum was chosen as the substrate material. Cytec Fiberite, FM-73 epoxy adhesive, obtained in a supported, 210 gram per square meter film, was the chosen as the adhesive. AdTech procured the substrate and adhesive materials and used them to manufacture Double Notch Shear (DNS) test panels and sent the rest of the materials to Brooklyn Polytechnic University for their use.

6.1 Surface Preparation for the Double Notch Bonded Shear Test Specimens

The bonded, DNS test specimens were manufactured as shown in Figure 2. Surface preparation of the aluminum adherends (Table 3) was conducted prior to bonding with the FM 73 adhesive. The cure cycle for the test panels was based upon recommendations by Cytec Fiberite, Inc. for their FM 73 film adhesive. A programmable oven with $\pm 1^\circ\text{C}$ temperature accuracy was used to cure the specimens. A special fixture held the two adherends in place while they were cured in the oven. The adhesive cure cycle consisted of: 1) ramp from RT to 110°C at $5^\circ\text{C}/\text{min}$; 2) isothermal cure at 110°C for 3 hours; and 3) cool back to RT.

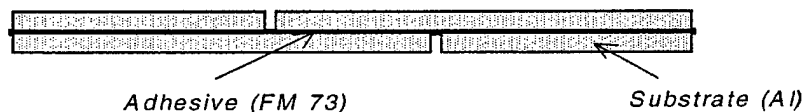


Figure 2. Double notch shear test specimen (length = 3.25"; width = 0.5"; thickness = 0.3125")

Table 3. Surface preparation for aluminum adherends

Sand the aluminum surface with 180 grit, silicon carbide paper and rinse with acetone.
Wipe the surface clean using Kim-Wipe and rinse again with acetone.
Wipe again until no grease is detected.
Immerse the specimen in 2M NaOH solution for 5 minutes.
Rinse the specimen with deionized water and check for water break.
Immerse in FPL solution for 10 minutes.
Spray rinse with de-ionized water.
Immerse in cold, de-ionized water and repeat spray rinse.
Check for water break and then dry in a vented oven at 50°C for 1 hour.
Store the freshly prepared samples in a desiccator until bonding. Bond within 72 hours after the surface preparation.
Spray rinse with de-ionized water.
Immerse in cold, de-ionized water and repeat spray rinse.
Check for water break and then dry in a vented oven at 50°C for 1 hour.
Store the freshly prepared samples in a desiccator until bonding. Bond within 72 hours after the surface preparation.
NOTES: If water does not break free in step #8, then repeat steps 5 to 7 until water breaks free.

Forest Products Laboratory Solution:

| | |
|--|---|
| Sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) | 17 grams |
| Sulfuric Acid (96% H_2SO_4) | 152 grams (82.6 ml of 96% H_2SO_4) |
| Aluminum 2024 | 0.75 grams |
| Ultra pure Water | Added to make 500 ml of solution |

AdTech manufactured sixteen 3.0" x 3.5" x 0.32" double notch shear test panels. The glass transition temperature (T_g) for the adhesive was determined to be 106°C using Differential Scanning Calorimetry. Five DNS specimens were extracted from each of these panels for a total of eighty double notch shear test specimens. Panels #1, #2, #5, #6, and #8 were utilized to develop proper surface preparation techniques. Panels #3, #10, #11, #12, #13, #14, #15 and #16, were manufactured using the Forest Products Laboratory (FPL) etch with no dead weight on the panels, while panels #4, #7, #9 were manufactured utilizing the FPL surface etch with 4.75 lbs of dead weight. The DNS specimens were numbered Sx-1 to Sx-5, where x was the bonded plate number.

6.2 Surface Preparation of the Fourier Transform Infrared Spectroscopy Specimens

These same materials were then supplied to Brooklyn Polytechnic so they could manufacture the Dielectric Relaxation Spectroscopy (DRS) and Fourier Transform Infrared (FTIR) bonded test specimens. Unfortunately, however, the adhesive film procured by AdTech was unable to be used by Brooklyn Polytechnic for their Dielectric Relaxation Spectroscopy studies. This was

because the carrier cloth within the adhesive complicated the resulting DRS spectra and it's subsequent analysis. Therefore, the same adhesive, in an unsupported film, known as FM 73U, was procured by AdTech from Cytec Fiberite and shipped to Brooklyn Polytechnic for their use.

The surface preparation techniques for the DRS and FTIR specimens, Figure 3, were slightly different than those used by AdTech. Polytechnic's five mm, round, aluminum disc samples were first polished with emery paper, degreased with acetone, and assembled using FM 73U. The adhesive thickness of the DRS test specimens was 0.05 mm and was controlled by inserting glass fibers between the two five mm discs prior to cure. However, two layers of adhesive were applied to the test specimens in the manufacture of the moisture-conditioned specimens. This was done to increase the amount of moisture pickup by the test specimens. The cure cycle utilized for the Polytechnic test specimens was based on Differential Scanning Calorimetry (DSC) data. The differential scanning calorimetry test was conducted with a Perkin Elmer Model DSC 7 in a nitrogen atmosphere. The DSC samples were scanned at 5°C/min from -40°C to 200°C to determine the T_g. The DSC thermogram revealed that the cure exotherm levels off after about 40 min at 110°C. Based on that data, the recommended cure cycle for the Polytechnic test specimens was: ramp at 5°C/min from RT to 110°C and then isothermal cure at 110°C for 60 minutes. Following cure, all specimens were placed into a dessicator and allowed to cool to room temperature for 60 minutes.



Figure 3. DRS and FTIR test specimens

7.0 ENVIRONMENTAL EXPOSURE OF BONDED JOINT TEST SPECIMENS

7.1 Environmental Exposure of the Double Notch Shear Bonded Joint Test Specimen

The DNS test specimens were placed in a controlled humidity chamber at the Materials Directorate, Air Force Research Laboratory, Wright Patterson Air Force Base. A weighing scale with a display accuracy of 0.0001 grams was utilized to measure moisture weight gain by the adhesive system. Before being placed in the environmental chamber, specimens were put in a vacuum oven for 15 minutes at 90°C. This was to ensure that the specimens were totally dry before weighing. It was assumed that the aluminum adherends did not gain weight, and hence, all weight gain was assumed to be moisture pickup by the adhesive. Moisture absorption was monitored during the exposure period for each set of temperature/humidity conditions, but moisture absorption curves were not generated. Each set of test specimens was placed in the

environmental chamber for a total of 184 hours. Additionally, two other sets of test specimens were exposed to the 60°C, 62% and 98% relative humidity environment for 312 hours. These tests were conducted in order to verify that the test specimens were actually saturated after 184 hours exposure time. Since the specimens saturated for 312 hours had the exact same weight gain as the specimens exposed for 184 hours, the specimens were assumed to be saturated within the 184-hour time frame.

7.2 Environmental Exposure of the Dielectric Relaxation Spectroscopy Test Specimen

Brooklyn Polytechnic however did not have access to a controlled humidity chamber. Hence, they utilized the following conditions to create their humidity environments. For the 50% relative humidity condition, Polytechnic used a saturated NaHSO_4 solution; for the 98% relative humidity condition, they used a solution of $\text{CuSO}_4 \times 5 \text{ H}_2\text{O}$ salt. Since Polytechnic exposed some specimens to full saturation in the humidity environments of 60 and 98 percent, these data could then be used to correlate the DRS data with the mechanical property data generated by AdTech.

The rate of moisture absorption by an adhesive is a function of relative humidity (RH), time and temperature of exposure to environment, and the structure of the adhesive. To facilitate comparison of mechanical and dielectric results, Polytechnic conducted measurements of the weight gain as a function of exposure time. Weight gain (WG) was calculated from: $(\text{WG}) = (W_t - W_0) / (W_f - W_0)$, where W_0 is the initial weight, W_t is the weight at time t of exposure to RH, and W_f is the final weight of a sample (the equilibrium weight of fully saturated sample). On the plot of the ratio $(W_t - W_0) / (W_f - W_0)$ vs. $t^{1/2}$, the slope can be used to calculate the coefficient of Fickian diffusion. The calculated value was determined to be $\sim 8 \times 10^{-8} \text{ cm}^2/\text{s}$ for the 98% RH at 70°C, which is in good agreement with the literature. Most important, however, is the fact that such a plot will enable direct comparison of the dielectric and mechanical test results using weight gain as a common denominator, thus eliminating the dependence on the specimen shape and size.

The DNS specimens exposed in the humidity chamber had weight gains of approximately 0.20 to 1.0 milligrams. Actual weight gains for the moisture saturated DNS test specimens exposed to a 62% RH environment, after 184 hours at RT, 60°C and 82°C, were 0.0002, 0.0003, and 0.0005 grams respectively. The weight gains for the DNS test specimens exposed to the 98% RH environment, after 184 hours at RT, 60°C and 82°C, were 0.0004, 0.0005 and 0.0010 grams respectively. Weight gain for the 60°C and 62% and 98% relative humidity levels after 312 hours of exposure were 0.0003 and 0.0005 grams respectively.

8.0 FOURIER TRANSFORM INFRARED SPECTROSCOPY TESTING

Fourier Transform Infrared Spectroscopy was performed using a Nicolet IR System 750 Spectrometer with spectral range from 15,800 to 50 cm^{-1} and the vectra scanning interferometer with a better than 0.1 cm^{-1} resolution. Near infrared data were obtained using a calcium fluoride beam splitter, a white light source and a MCT detector. All spectra were measured at 4 cm^{-1} resolution using 64 scans. The optical fiber probe was immersed directly in the sample, which was located inside a glass tube. The spectral region between approximately 4,000 and 7,100 cm^{-1} was investigated in this study.

An uncured adhesive sample was placed in the sample cell, and a near-IR (NIR) spectrum was obtained. The sample was then heated to 110°C. After curing, a NIR measurement was done again. Finally, the sample was exposed to the humid environment, and the measurements were taken at selected time intervals.

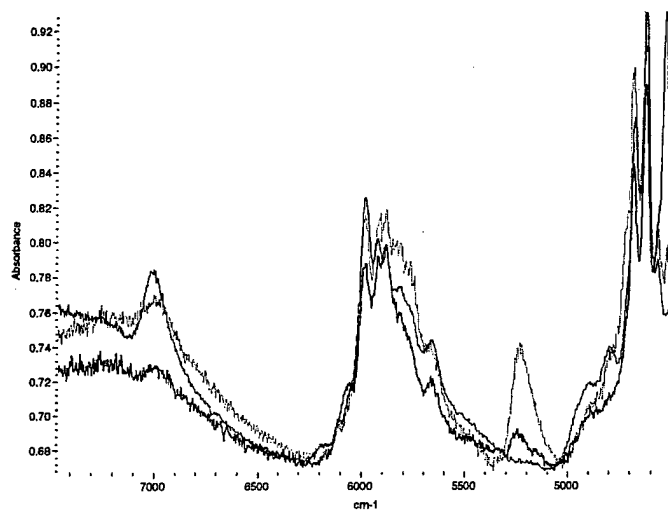


Figure 4. FTIR spectra of as-received (red line), dry (green line) and moist (black line) samples

A comparison of these spectra revealed three major differences caused by the absorbed moisture. These differences are the result of hydrogen bonding between the water molecules and -OH groups in the matrix, and are manifested as an effect on the following characteristic peaks.

- 1) 5240 cm^{-1} , -OH stretching vibration of water molecule
- 2) 7000 cm^{-1} , -OH stretching vibration, - The peak shifts to lower wavenumber, and broadens by hydrogen bonding
- 3) 4900~4800 cm^{-1} , -OH Combination Band.

The determination of glass transition, T_g , is an essential characterization step for this analysis, since the molecular motion above the T_g is different from that below the T_g . Differential Scanning Calorimetry (DSC) is a well-established method for determination of T_g . DSC experiments were performed on the Perkin Elmer Model DSC-7 instrument. Approximately 10 mg of sample was deposited in the aluminum pan, and the heating rate of 10°C/min was applied. The DSC glass transition temperature, T_g , was determined as the temperature corresponding to half of the heat capacity change. As-received, dry and humidity-aged samples resulted in glass transition temperatures of 6.8°C, 92.7°C and 81.2°C respectively. Glass transition temperature generally increases with curing, as the segmental motion becomes increasingly restricted by cross-linking (network formation). The glass transition temperature of humidity aged samples are, however, usually below those of dry samples, as recorded here.

9.0 DIELECTRIC RELAXATION SPECTROSCOPY TESTING

In Task 4, Brooklyn Polytechnic utilized the Dielectric Relaxation Spectroscopy (DRS) technique on as-received, dry, and humidity aged test specimens. Polytechnic's facility for dielectric measurements consisted of modified commercial instruments: a Solartron 1260 Impedance Gain Phase Analyzer (10 μ Hz - 32 MHz) and a Hewlett Packard 4291A RF Impedance Material Analyzer (1 MHz - 1.8 GHz). Each instrument has a temperature-controlled chamber and is interfaced to a computer via a National Instrument IEEE 488.2 interface bus. The resulting data are presented in the frequency domain in terms of the complex dielectric loss $\epsilon^*(\omega)$ with temperature as a parameter. The overall goal of this portion of the program was to provide quantitative characterization of water/adhesive interactions. Moisture in the adhesive affects not only its permittivity, as it has been established by other investigators, but also dielectric loss.

For the dielectric relaxation tests, Brooklyn Polytechnic first examined an adhesive specimen in the uncured, as-received condition. This data then served as a reference. The results are presented in the frequency domain in terms of both the dielectric constant (the real part of the permittivity) and the dielectric loss (the imaginary part of the permittivity). Dielectric constant and loss for the as-received sample, with temperature as a parameter, are shown Figures 5a and 5b. The temperature region was between 30°C and 80°C, hence well above the calorimetric glass transition temperature of the uncured adhesive, determined to be approximately 7°C. (The observed relaxation is the α process, which is caused by the segmental motion of epoxy molecules.) This relaxation process shifts to lower frequencies with decreasing temperature.

The adhesive sample was cured at 110°C and then placed in a desiccator for 60 minutes. Following this procedure, a DRS spectrum was obtained at 24°C. The temperature was then increased to 30°C and another DRS spectrum was obtained. This procedure continued increasing the various temperatures to 40°C, 50°C, 60°C, 70°C, 80°C, 90°C, 100°C and 110°C. A plot of dielectric constant and loss (ϵ'') versus frequency was obtained with temperature as a parameter as shown in Figures 6a and 6b. The frequency range utilized for this testing spanned from 1.00E-02 to 1.00E+08. Low frequency data, Figure 6a, is considered to range from 1.00E-02 to 1.00E+06 and was conducted using a low frequency machine. High frequency data, Figure 6b, was conducted using a different, machine, is considered to range from 1.00E+06 to 1.00E+08.

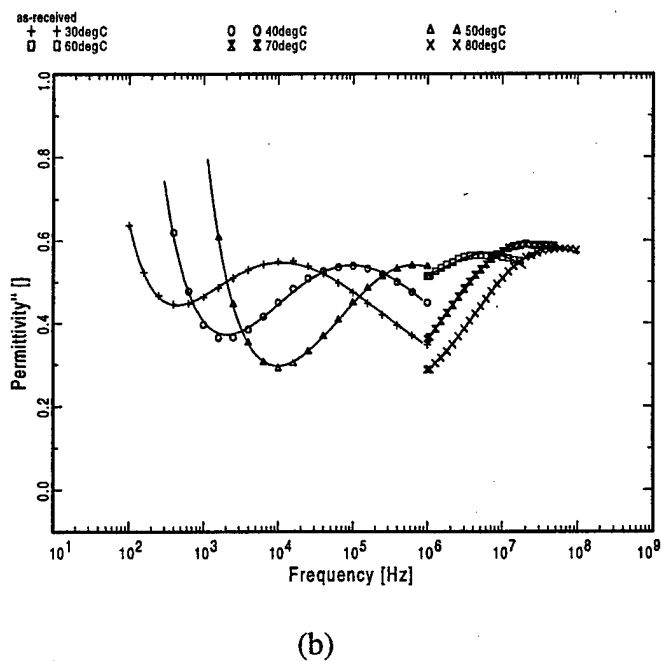
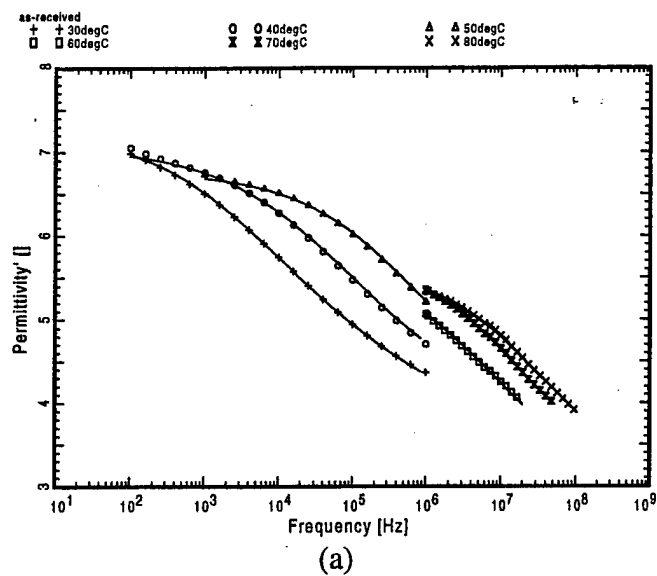
There is only one dielectric relaxation peak for the dry specimen in either the low or the high frequency range. The peak occurs from 1.00E+02 to 1.00E+05 for the low frequency range and from 1.00E+07 to 1.00E+08 for the high frequency range. In both cases, this relaxation peak changes as the temperature changes. These changes include 1) an increase in intensity as the temperature increases; 2) a shift in the curves toward higher frequencies as temperature increases; and 3) sharper and more defined relaxation peaks as the temperature increases.

The position of the peak maximum in the frequency domain (f_{\max}) defines the characteristic relaxation time τ_{\max} ($\tau_{\max} = 1/\omega_{\max} = 1/(2\pi f_{\max})$). Lower frequency peaks correspond to longer relaxation times, since the frequency of the peak is the reciprocal of the relaxation time. The relaxation peak for the dry sample is related to reorientational movement of the hydroxyl groups

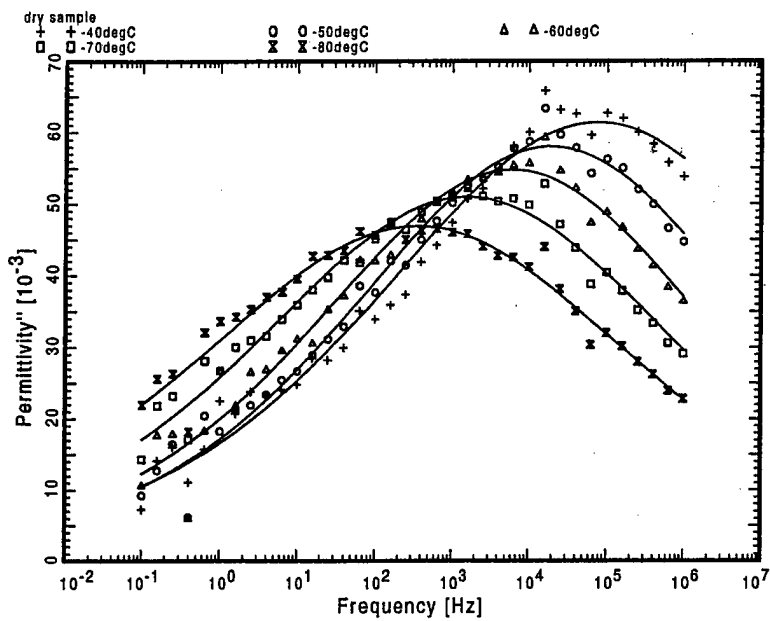
in the cured epoxy adhesive (β -relaxation process). It was anticipated that this relaxation peak should be affected by absorbed moisture via interactions with hydroxyl groups. The reorientational motions of dipoles, due mostly to the hydroxyl groups, are at the origin of the β process.

High frequency, dielectric spectroscopy testing was then conducted on specimens exposed for 15 hours at 50% relative humidity at 24°C. The samples were immediately transferred from the environment to the sample cell. This data, shown in Figure 7, shows the same trend as for the dry specimens, that is, that the permittivity loss increases with increasing temperature, the curves shift to higher frequencies with higher temperatures, and the peaks of the curves become sharper with higher temperatures.

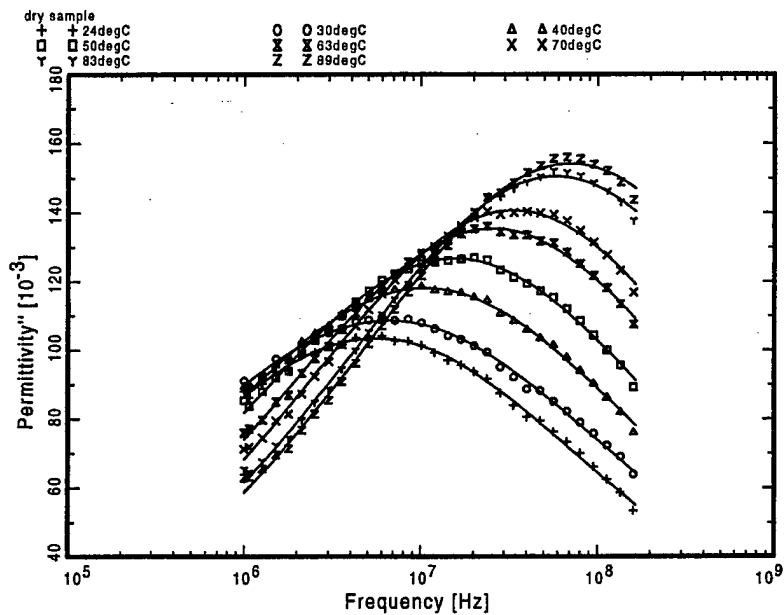
Tests were then conducted on specimens exposed for 720 hours at 98% relative humidity (RH) and 24°C. This data, shown in Figure 8, reveals similar trends. Tests were also conducted on the heavily exposed specimens, 90 hours at 98% RH and 70°C, shown in Figure 9. These data also exhibit similar trends, although there appears to be a second peak in the high frequency region for those tests conducted at the lower temperatures (24°C - 70°C).



Figures 5a & b. Dielectric constant (a) and loss (b) in the frequency domain for various temperatures for the FM 73 adhesive in the as-received condition



(a)



(b)

Figures 6a & b. Dielectric loss of the FM 73 adhesive in the dry condition at low (a) and high (b) frequencies

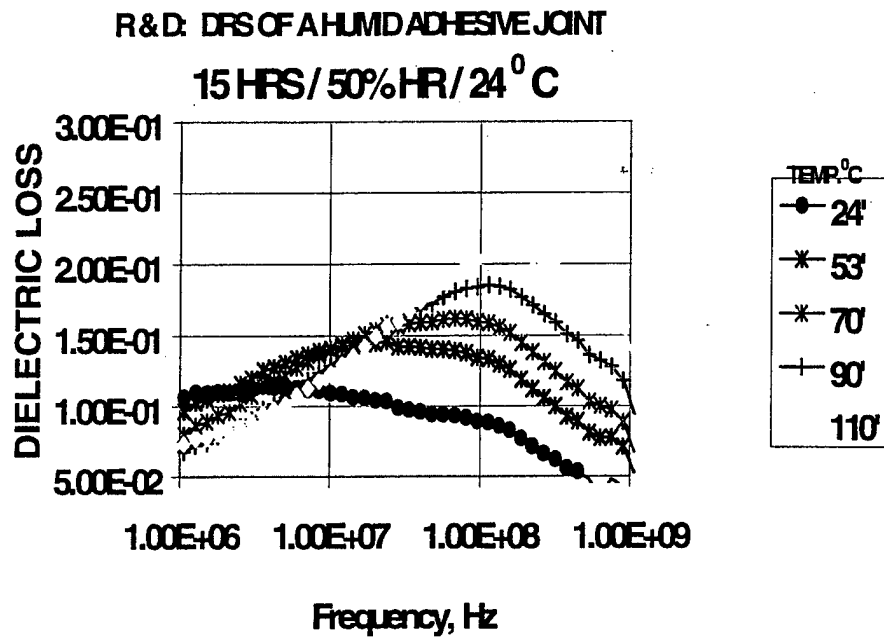


Figure 7. DRS spectra, at various temperatures, for an adhesive bond joint exposed for 15 hours at 50% relative humidity and 24°C

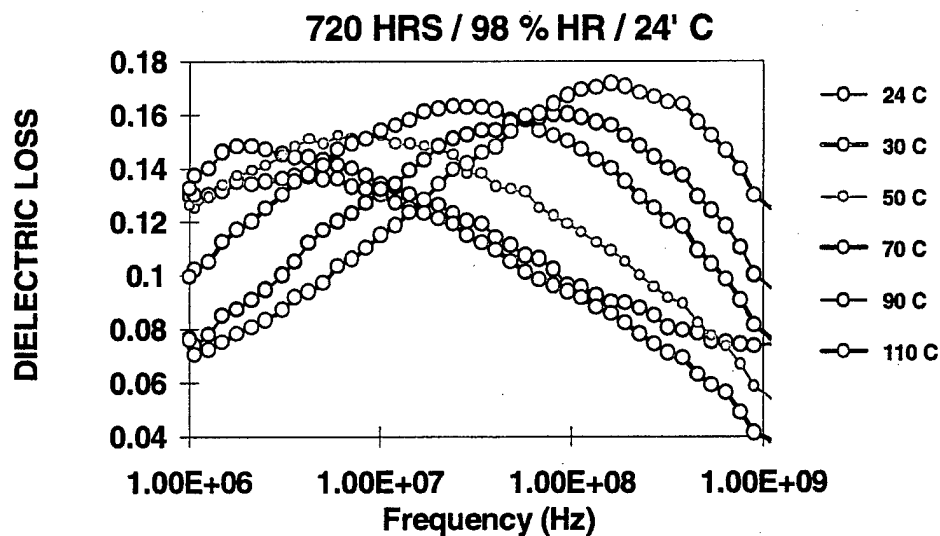


Figure 8. DRS spectra, at various temperatures, for adhesive bond joint exposed for 720 hours at 98% relative humidity and 24°C

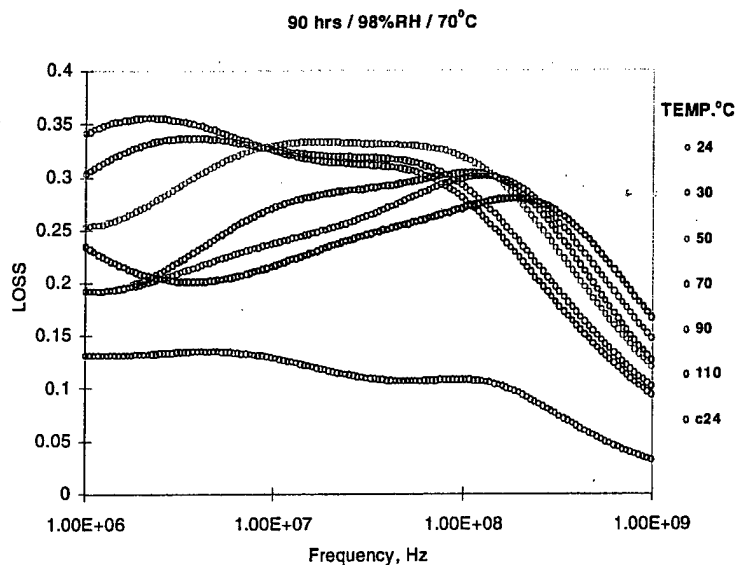
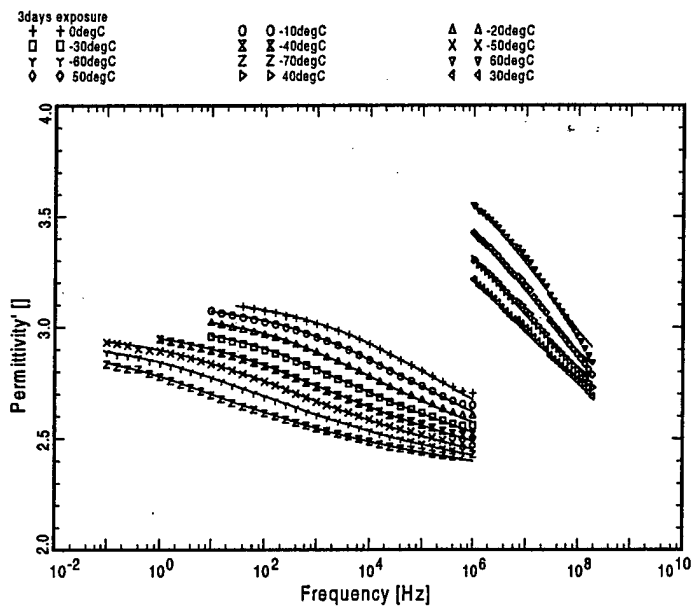
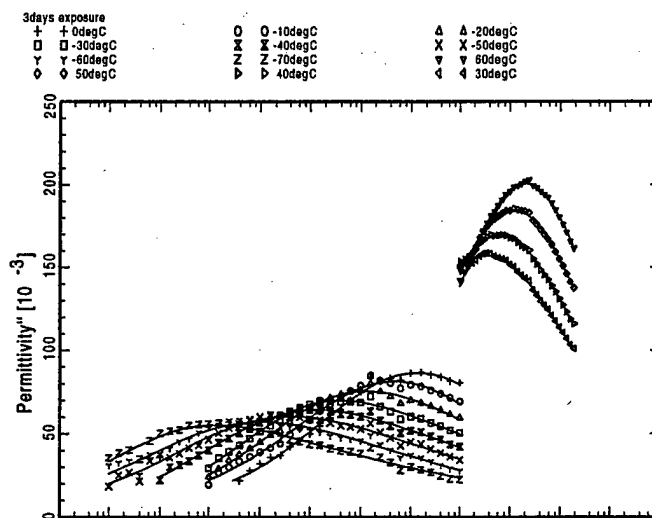


Figure 9. DRS spectra, at various temperatures, of an adhesive bond joint exposed for 90 hours at 98% relative humidity and 70°C

The rest of the DRS testing was conducted on specimens exposed to 60°C and 98% relative humidity. Initially, it was determined that moisture saturation occurred after 6 days of humidity exposure. For this portion of the test matrix, moisture levels in the specimens were lower than saturation levels. DRS testing was conducted after 3 days (72 hours) exposure to 60°C and 98% relative humidity, 5 days (120 hours), and 10 days (240 hours) exposure respectively. DRS spectra were obtained on the specimens starting at 60°C temperature (where the moisture saturation occurred) and continued to lower temperatures, usually -70°C or -80°C. For these tests, both low and high frequency data were obtained. Figures 10a, 10b, 11a, 11b, 12a and 12b depict this data.

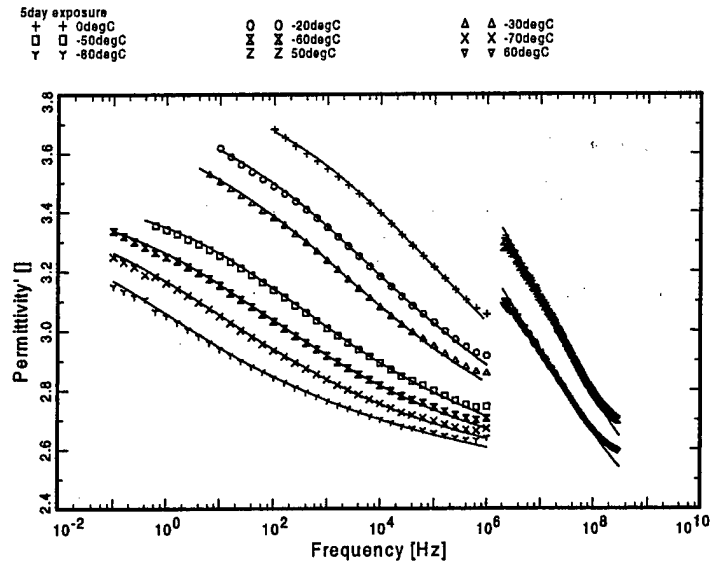


(a)

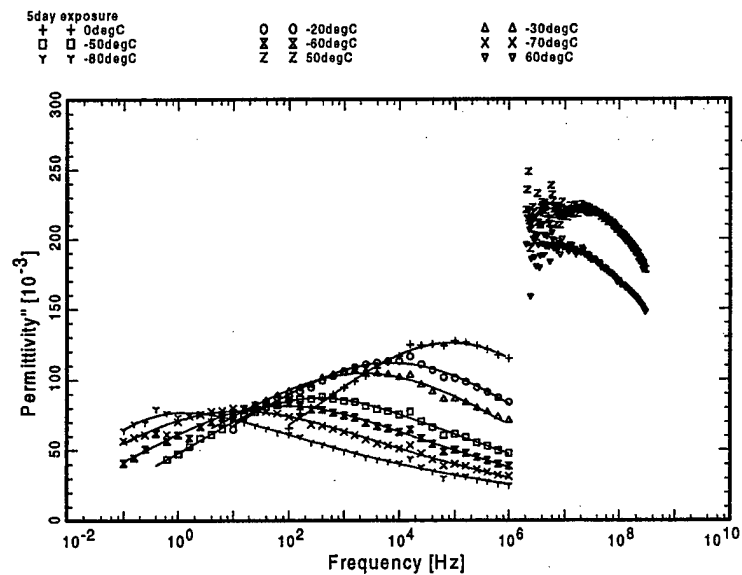


(b)

Figures 10a & b. Dielectric constant (a) and loss (b) in the frequency domain at various temperatures for specimens exposed for 3 days at 60°C and 98% relative humidity

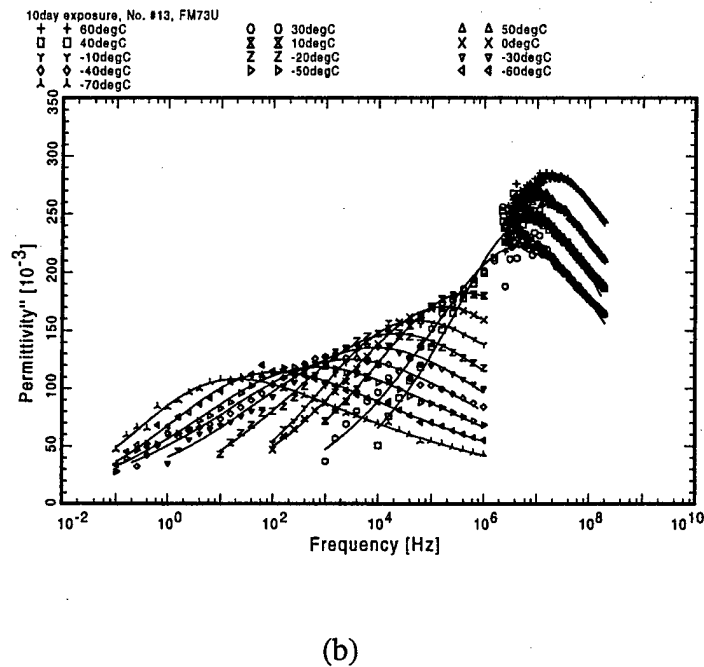
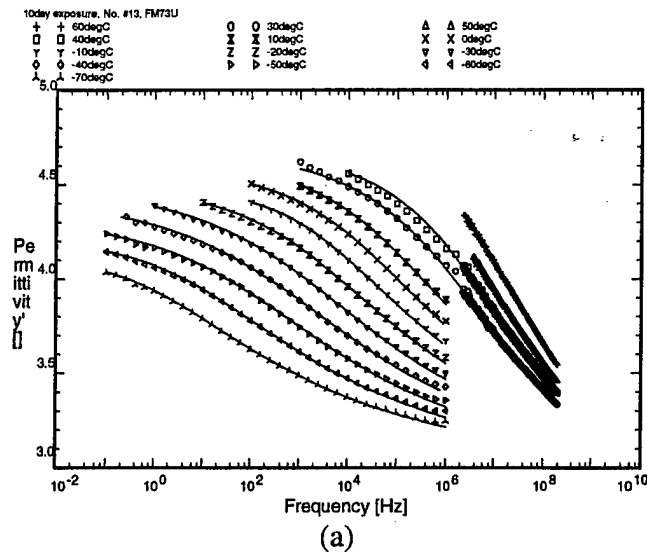


(a)



(b)

Figures 11a & b. Dielectric constant (a) and loss (b) in the frequency domain for various temperatures for specimens exposed for 5 days at 60° C and 98% relative humidity



Figures 12a & b. Dielectric constant (a) and loss (b) in the frequency domain at various temperatures for specimens exposed for 10 days at 60°C and 98% relative humidity

10.0 MECHANICAL TESTING OF ADHESIVELY BONDED JOINTS

For each double notch shear specimen, the average thickness, width and length of the bonded region were initially recorded. The specimens were then dried out and exposed to the hygrothermal environments identified in Table 4. Weight gain was recorded throughout the exposure period. After the final weighing, the specimens were returned to AdTech for subsequent testing within the hour. The DNS specimens were then subjected to axial compression loads per ASTM D 3846-94. For this test, the specimens were loaded edgewise in a supporting jig of the same description as referenced in ASTM D 695. The load versus stroke data for each case was obtained from a computer linked to the test frame. The ultimate failure load was also noted for each test specimen. Following failure, specimens were examined and failure modes identified. Shear strength values (psi) were then calculated as the failure load (pounds) divided by the total failure area (inch²). Any factor, such as gross porosity in the bonds, known to affect the failure load or mode, was also noted and recorded since this information could significantly affect test results.

From the table, it does appear that moisture absorption increases with higher temperatures and higher humidity levels. Weight gains for the 62% relative humidity samples at room temperature, 60°C, and 82°C were 0.0002, 0.0003 and 0.0005 grams respectively. For the specimens exposed to 98% relative humidity at room temperature, 60°C and 82°C, the weight gains were 0.0004, 0.0005 and 0.0010 grams respectively. Shear strength values for the 62% relative humidity specimens ranged from 4525 psi to 5408 psi. Shear strength values for the 98% relative humidity conditions ranged from 4786 psi to 5502 psi. Regarding failure modes, it was determined that the lower moisture levels (0.0000 to 0.0004 gr) generally resulted in cohesive failure of the adhesive, that is failure within the adhesive itself. Specimens which absorbed higher moisture levels, 0.0005 grams and up, resulted in mostly adhesive, or adhesive/adherend interfacial failures. Specimens, which absorbed moisture in the range of 0.0004 to 0.0005 grams sometimes, exhibited mixed failure modes. This mixture of failure modes means that some specimens exhibited some adhesive and some cohesive failure within a specimen or that specimens tested under the same conditions, exhibited both adhesive and cohesive failures.

Table 4. Weight gain, failure mode and ultimate shear strength of the double notch shear test specimens after exposure to a hygrothermal environment

| Temp⇒ Humid⇓ | Room Temperature 184 hours | 60°C 184 hours | 82°C - 184 hours or 100°C Boiling Water- 24 hours | 60°C 312 hours |
|-----------------|--|---|--|---|
| 15 % | s-4 Wt Gain = None Failure =Cohesive Strength=6319 psi | N/A | N/A | N/A |
| 62 % | s-15 WtGain=0.0002 gr Failure =Cohesive Strength=4973 psi | s-12 WtGain=0.0003gr Failure =Cohesive Strength=4525 psi | s-11 WtGain=0.0005gr Failure=Adhesive Strength=4727 psi | s-10 WtGain=0.0003gr Failure =Cohesive Strength=5408 psi |
| 98% | s-9 WtGain=0.0004 gr Failure =Cohesive Strength =5502 psi | s-16 WtGain=0.0005gr Failure =Mixture Strength=5267 psi | s-14 WtGain=0.0010gr Failure =Adhesive Strength=4938 psi | s-13 WtGain=0.0005gr Failure =Adhesive Strength=4786 psi |
| BoilingWater | N/A | N/A | s-7 WtGain=0.0065gr Failure =Mostly Adhesive Strength=3598 psi | N/A |

10.1 Baseline Double Notch Shear Mechanical Property Data

The baseline, in-plane shear strength was established by testing ten (10) unexposed DNS specimens under axial compression loading. The average failure load of the first set of five DNS specimens was found to be 6319 ± 148 psi and 6076 ± 351 psi for the second set. These values agree with the value of 6250 psi provided in literature by Cytec Fiberite, Inc. The failure mode for these specimens was determined to be cohesive within the adhesive. A plot of the load versus stroke data for one of these two sets of DNS specimens is shown in Figure 13. The consistency of the experimental data is good. From this data, it can be seen that the FM73 adhesive exhibits nonlinear material behavior. The nonlinear behavior of the FM73 adhesive is predominantly bilinear in nature. Additionally, on average, the DNS specimens seem to carry an additional load of over a 100 pounds after the elastic limit.

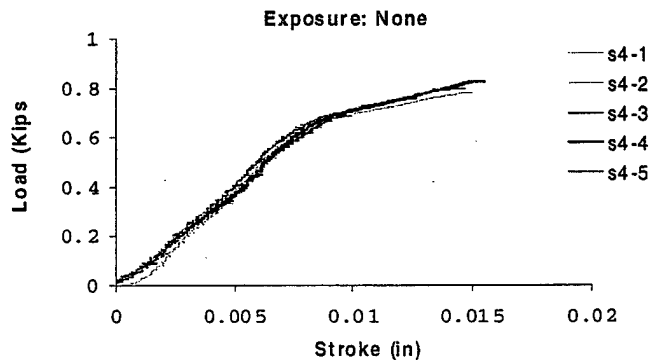


Figure 13. Load versus stroke data for the unexposed DNS specimens

10.2 Double Notch Shear Test Results after Exposure to a Harsh Environment

Five, double notch shear specimens were also exposed to a "harsh environment" by placing them in boiling water for 24 hrs. The average moisture gain by weight for these specimens was approximately 0.0065 grams. These specimens were tested under static compression load within one hour after removing them from the boiling water. The observed mode of failure was mostly at the adhesive/aluminum interface, suggesting moisture ingress at that location. The average ultimate shear strength was determined to be 3598 ± 449 psi. The load versus displacement curves for these five specimens are shown in Figure 14. Except for one specimen, the experimental data is reasonably consistent. These specimens carry a very small load after the elastic limit. These specimen curves also exhibit considerably reduced displacement prior to failure as compared to the non-exposed specimens.

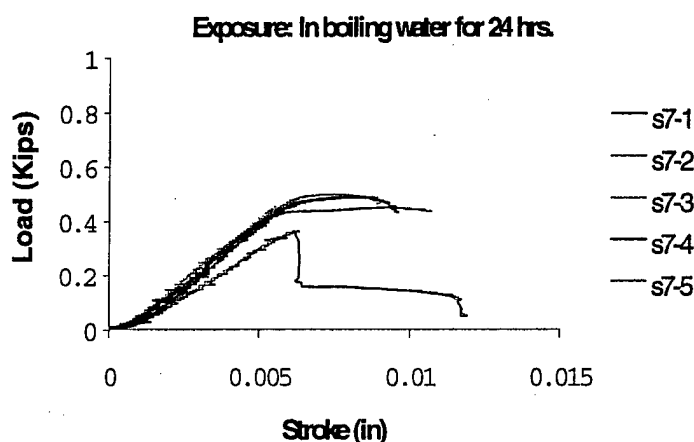


Figure 14. Load versus stroke data for DNS specimens after immersion in boiling water for 24 hours

10.3 Double Notch Shear Test Results after Hygrothermal Exposure for 184 hours at 62% Relative Humidity at RT, 60°C and 82°C

Fifteen double notch shear (DNS) specimens were then exposed to 62% relative humidity, five at each of three different temperatures (RT, 60°C and 82°C) for 184 hrs per exposure. The average weight gain for each set of specimens exposed to the above humidity/temperature conditions was 0.0002 grams, 0.0003 grams, and 0.0005 grams respectively. These specimens were then tested under static compression within one hour after removing them from the environmental chamber. Failure modes ranged from cohesive failure for the 62% relative humidity, room temperature and 60°C tests, to adhesive failure for the 62% relative humidity, 82°C test. The average ultimate shear strengths were determined to be 4973 ± 298 psi for the room temperature specimens, 4525 ± 795 psi for the 60°C specimens and 4727 ± 161 psi for the 82°C specimens. The load versus displacement curves for these three sets of data are shown in Figures 15, 16, and 17.

The consistency of the experimental data is not as good in these cases. The three, load versus displacement curves with the lowest ultimate loads for the 62% relative humidity, 60°C specimens (Figure 18) were thought to be the result of a significant amount of porosity in these particular adhesive bond specimens. For the room temperature and 60°C exposures, the compression stress-strain curves for the FM 73 adhesive are predominantly bilinear in nature. When comparing the exposed specimens (Figures 15 and 16) to the unexposed specimens (Figure 13), however, the slope of the second part of the bilinear response is noted to be much smaller. These specimens also appear to have a reduced load carrying capability after the elastic limit, indicating more "plasticity" in the humidity aged samples. This "enhanced plasticization" after moisture intrusion has been reported in the literature by other researchers as well. It also appears that the specimens with the greatest amount of moisture intrusion (those exposed at 82°C, Figure 17) exhibit a little less strain before failure than the other specimens. These latter specimens were also noted to have failed adhesively as compared to the cohesive failure mode exhibited by the other two sets of humidity aged specimens.

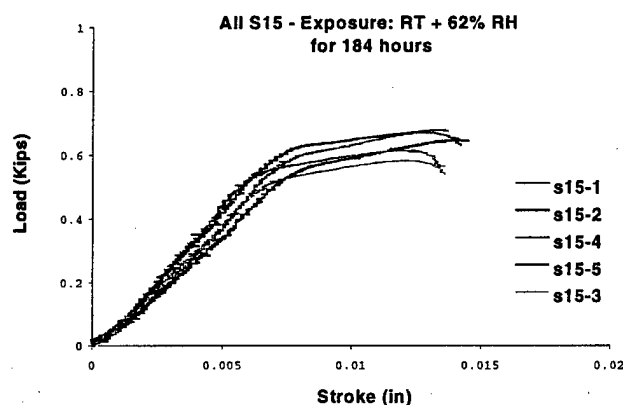


Figure 15. Load versus stroke data for DNS specimens after exposure to 62% relative humidity and room temperature for 184 hours

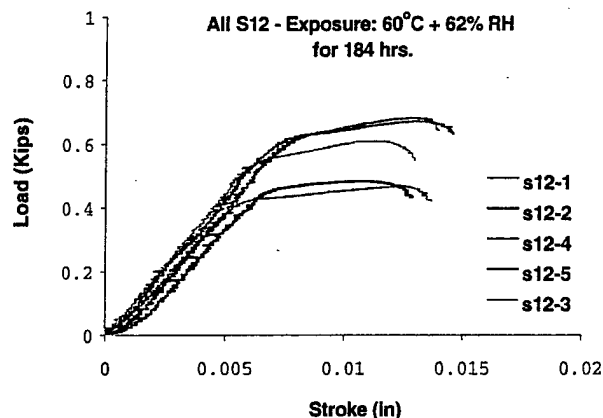


Figure 16. Load versus stroke data for DNS specimens after exposure to 62% relative humidity and 60°C for 184 hours

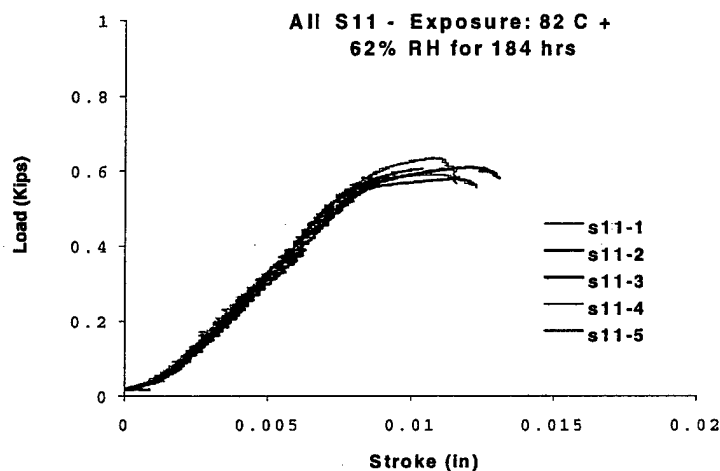


Figure 17. Load versus stroke data for DNS specimens after exposure to 62% relative humidity and 82°C for 184 hours

10.4 Double Notch Shear Test Results after Hygrothermal Exposure for 184 hours at 98% Relative Humidity at RT, 60°C and 82°C

Fifteen double notch shear (DNS) specimens were then exposed to 98% relative humidity conditions, with five specimens again exposed at each of three different temperatures (RT, 60°C and 82°C) for 184 hrs. In this case, the recorded weight gains were 0.0004 grams, 0.0005 grams, and 0.0010 grams respectively. Failure modes ranged from cohesive failure for the room

temperature test specimens, to a mixture of cohesive and adhesive failure for the 60°C test specimens, to adhesive failure for the 82°C test specimens. Again, adhesive failure at the adhesive/aluminum interface suggests moisture ingress at the adhesive/aluminum interface. The ultimate shear strengths were determined to be 5502 ± 382 psi for the RT specimens, 5267 ± 359 psi for the 60°C specimens, and 4938 ± 204 psi for the 82°C specimens. The load versus displacement data for the 98% relative humidity specimens, Figures 18 - 20, are similar to the load versus displacement data for the 62% relative humidity specimens.

Again, the consistency of the experimental data is good, with the stress-strain curves exhibiting predominantly bilinear material behavior for the two lower temperature exposures. In comparing the exposed specimens to the unexposed specimens (Figure 13), it was again noted that the slope of the second part of the stress strain curve for the humidity exposed specimens is lower. This indicates that these specimens have a reduced load carrying capability after the elastic limit, indicating a "plasticizing" of adhesive after humidity exposure. Again, the failure mode changes from cohesive for the room temperature specimens, to a combination of cohesive and adhesive for the 60°C specimens, to the totally adhesive failure mode of the 82°C specimens. Additionally, there is again, a reduction in the amount of total plastic strain in the adhesive with the highest moisture level, where the failure mode is adhesive.

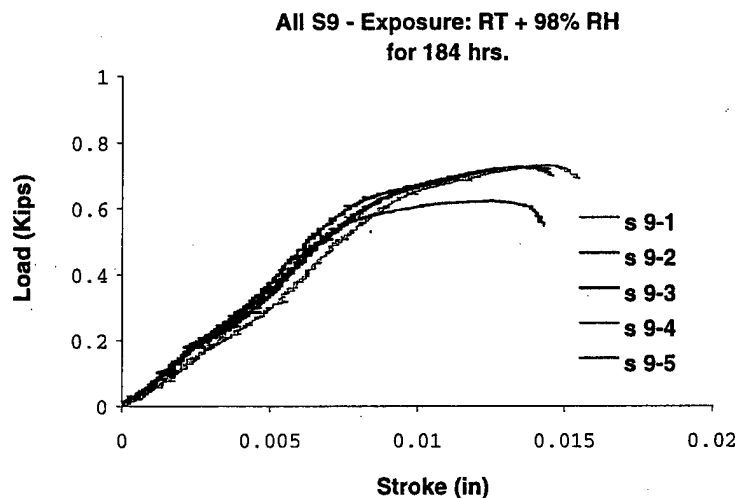


Figure 18. Load versus stroke data for DNS specimens after exposure to 98% relative humidity and room temperature for 184 hours

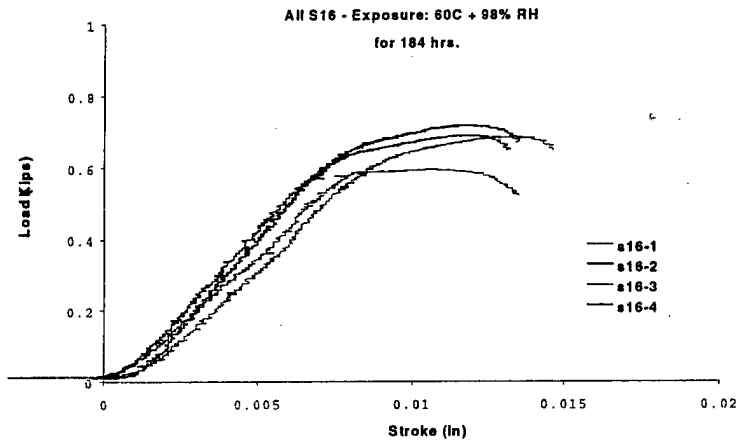


Figure 19. Load versus stroke data for DNS specimens exposed to 98% relative humidity and 60°C for 184 hours

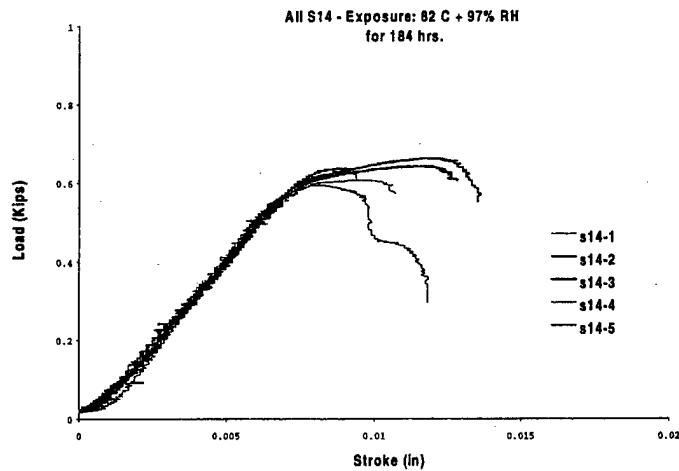


Figure 20. Load versus stroke data for DNS specimens exposed to 98% relative humidity and 82°C for 184 hours

10.5 Double Notch Shear Test Results after Hygrothermal Exposure for 312 Hours at 60°C and 62% and 98% Relative Humidity

The double notch shear specimens exposed to the 60°C, 62 and 98 percent relative humidity conditions for 312 hours exhibited behavior similar to the specimens exposed under the same conditions for 184 hours. The average weight gain for the 62% relative humidity samples was 0.0003 grams and for the 98% relative humidity samples, it was 0.0005 grams. The observed mode of failure for the 62% relative humidity, exposed specimens was essentially cohesive, whereas the observed mode of failure for the 98% relative humidity, exposed specimens was mostly adhesive. The average ultimate shear strength of the specimens exposed to 62% relative humidity was 5408 ± 373 psi, and for the specimens exposed to 98% relative humidity, it was 4786 ± 317 psi. The experimental data was reasonably consistent and the data exhibit the same trends noted previously.

10.6 Finite Element Analysis

AdTech also performed a 3-D finite element (FE) analysis of the DNS specimen configuration using the SDRC I-DEAS finite element package. The purpose of this analysis was to determine if the stresses in the double notch shear specimen were predominantly shear in nature. The adhesive stresses in the bonded region depict a pure shear deformation. Thus, the failure loads obtained from the mechanical tests can be interpreted as the apparent shear strength of the DNS bonded joint. The results of the finite element analysis are shown in Figure 21. As expected the prominent stress in the bonded region is the transverse shear stress component, τ_{xy} , whereas the transverse normal stress σ_{zz} , component is negligibly small in most of the bonded region. This analysis confirms that the failure in the bonded region will be shear dominant. Thus, the FE analysis concludes that failure loads obtained from the mechanical tests can be interpreted as the apparent shear strength of the DNS bonded joint.

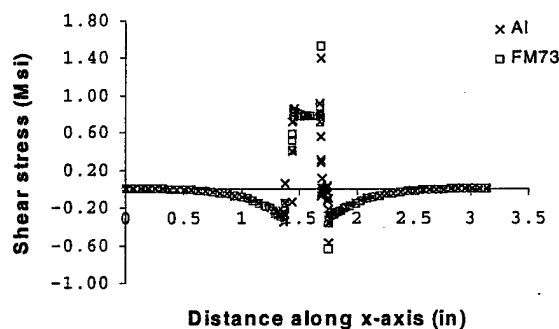


Figure 21. Shear stress in the DNS specimen at the substrate/adhesive interface

11.0 RESULTS

It is known that the molecular dynamics of epoxy resins and adhesives are changed by the presence of moisture. For example, the addition of moisture plasticizes resins and adhesives, lowers the glass transition temperature, and leads to degradation of mechanical properties. This program was aimed at identifying the local molecular motions in an epoxy network exposed to a humid environment. The elucidation of these changes in the adhesive network, as a result of absorbed moisture, is the key to understanding the microscopic response and failure of these materials.

11.1 Fourier Transform Infrared Spectroscopy Test Results

The Fourier Transform Infrared (FTIR) spectroscopy data, Table 5 below, indicate that the humidity aged samples exhibit several different features from the dry samples. Around 7000 cm^{-1} , the humidity aged samples have broader peaks than the dry samples and shift to lower wavenumbers. There is also a peak at the 5240 cm^{-1} for the humidity aged samples that was not evident in the dry sample. There is also just one peak at 4800 cm^{-1} for the humidity aged samples, whereas there were two peaks in this range for the dry samples.

Table 5. NIR peaks due to interactions of -OH group and water

| Location Sample | 7000 cm^{-1} | 5240 cm^{-1} | 4900 cm^{-1} $\sim 4800\text{ cm}^{-1}$ |
|--------------------|---|-----------------------|--|
| Pre-cure | No peak | Small peak | No peak |
| Dry | Sharp peak | No peak | Two peaks 4800 cm^{-1} & 4900 cm^{-1} |
| Humidity Aged | Broad peak Shifts to lower wavenumber | Large peak | One peak 4800 cm^{-1} |

11.2 Dielectric Relaxation Spectroscopy Test Results

The results of the dielectric relaxation spectroscopy tests are best seen by comparing the spectra for dry and humidity aged specimens. Figure 22 shows that the humidity aged specimens generally exhibit higher permittivity values than for the dry specimens. Additionally, higher moisture levels result in higher permittivity values. And, although similar trends are observed for the DRS data in the low frequency regime, another trend is also observed there. Shown in Figure 23, the humidity-aged specimens in the low frequency regime not only have an increase in the permittivity value, but there is a shift of the relaxation peak to lower frequency as compared to the dry sample. This shift is characteristic of the β process and is the first time that these effects were observed and quantified by broad band DRS.

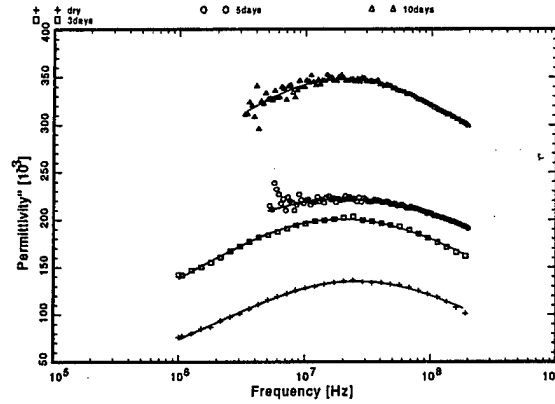


Figure 22. Dielectric loss in the high frequency domain for dry (lowest curve), 3-day exposure (next highest curve), 5-day exposure (next highest curve) and 10-day exposure (highest curve)

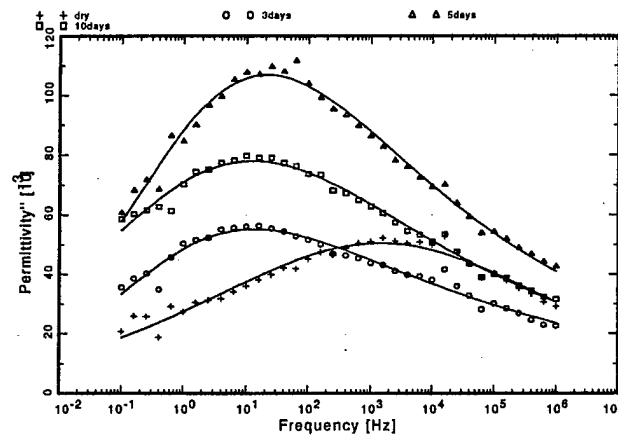


Figure 23. Dielectric loss in the low frequency domain for dry (lowest curve) and moist specimens at -70°C (10-day exposure for the top curve, 5-day exposure for the next lowest curve down, and 3-day exposure (for third curve down))

The dielectric relaxation spectroscopy data were analyzed by fitting the actual data to the Havriliak-Negami (HN) equation. This equation is commonly used to express the frequency dependence of the dielectric constant and loss. This equation is shown below

$$\epsilon(\omega) = \epsilon' - j\epsilon'' = \frac{\Delta\epsilon}{\{1 + (j\omega\tau_{\text{HN}})^{\beta}\}^{\alpha}} + \frac{\sigma_{\text{dc}}}{j\omega\epsilon_0}$$

where ϵ' is the real part of the complex permittivity, ϵ'' is the imaginary part of the complex permittivity; $\Delta\epsilon$ is the relaxation strength, τ_{HN} is the characteristic relaxation time of the Havriliak-Negami (HN) equation, ϵ_0 is the dielectric constant of vacuum, j is the imaginary unit and σ_{dc} is the dc conductivity. The variables α and β are the broadening shape factors.

The α process in the as-received sample and the β process in dry and moist samples were found to be well described by the HN equation. The dielectric parameters for each spectrum were determined and the resulting HN curve fits are shown as the solid lines in Figures 5 - 7 and Figures 10 - 12.

The relaxation strength, $\Delta\epsilon'$ of the individual relaxation process, depends on the dipole orientation (g), the dipole moment (μ), the dipole concentration (N) and the temperature (T). In the case of polymer chains we have:

$$\Delta\epsilon' = \epsilon_0 - \epsilon_\infty = \frac{4\pi N}{3kT} \left(\frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty} \right) \left(\frac{\epsilon_\infty + 2}{3} \right)^2 g\mu^2 \quad (2)$$

where ϵ_0 is the (static) permittivity at low frequency, ϵ_∞ is the dielectric constant as $\omega \rightarrow \infty$, g is g -factor to describe the structural arrangement of dipole, N is number of dipoles per unit volume, μ is dipole moment, k is Boltzman's constant, and T is temperature.

The dielectric relaxation strength, $\Delta\epsilon'$, plotted as a function of temperature, for the dry specimens and those saturated at 60°C and 98% relative humidity for 3, 5, and 10 days, reveals that relaxation strength decreases with decreasing temperature (Figure 24). Simultaneously, the relaxation peaks generally become broader (Figure 25) with increasing moisture content. These trends are characteristic of the β relaxation process.

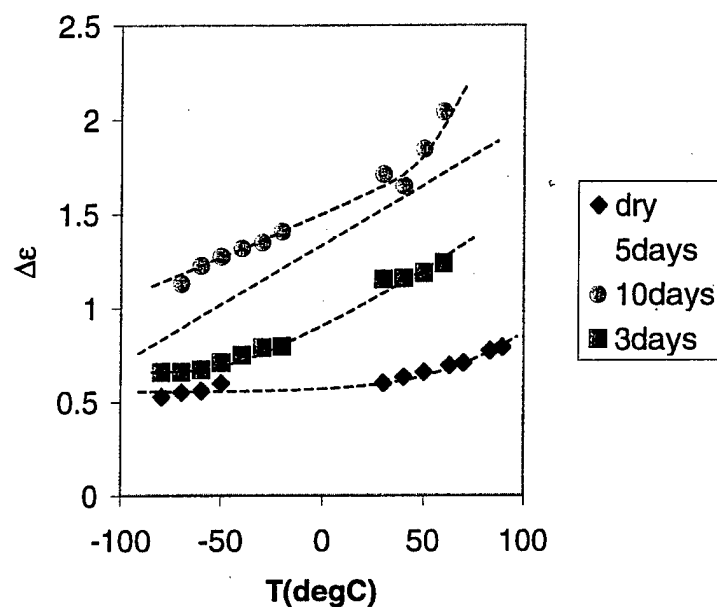


Figure 24. Relaxation strength for dry and moist samples as a function of temperature with exposure time as a parameter. (Moist specimens exposed to 60°C and 98% relative humidity for three different time periods)

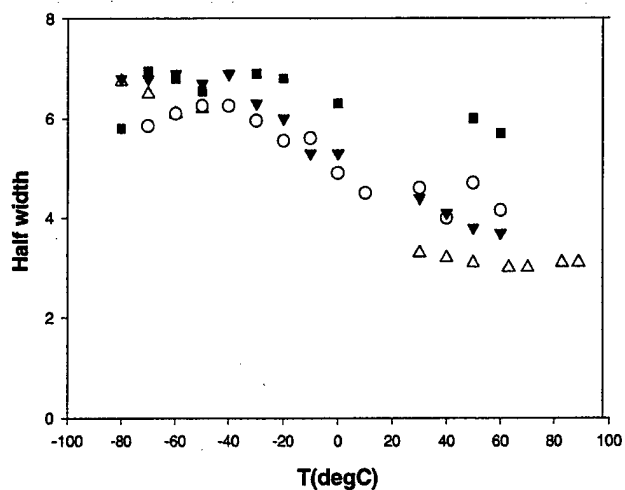


Figure 25. Half width of the relaxation peak for dry and moist samples as a function of temperature

Relaxation maps (Figure 26) were then constructed by plotting the relaxation time, $\tau = 1/(2\pi f_m)$, as a function of reciprocal temperature. This data would appear to indicate, that although the relaxation time of dry samples is affected by humidity aging, the different amounts of moisture in the specimens obtained by the different exposure times, does not affect the relaxation time further. This plot also depicts the apparent activation energy (which is related to the potential barrier necessary to orient the dipole) from the slope of curves. Analysis reveals the slope to be 41 kJ/mol for the dry sample and 60 kJ/mol for the moist samples. The larger activation energy of moist samples suggests that the local motion was restricted by the hydrogen bonding between the polar groups on the epoxy-amine network and the absorbed water.

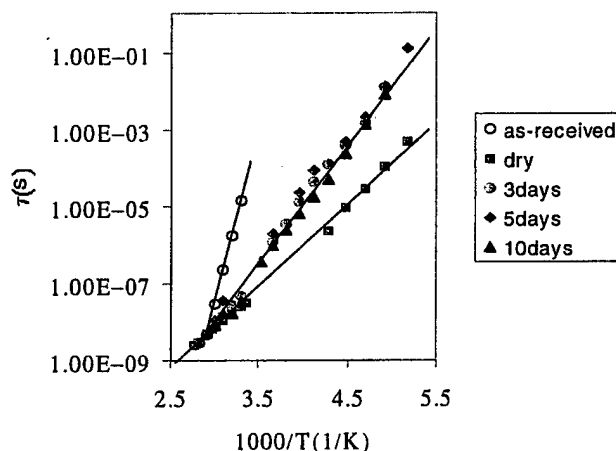


Figure 26. Arrhenius plots of the relaxation time for the as-received, dry and moist samples

11.3 Mechanical Property Data Test Results

The results of the mechanical property data reveal trends similar to those noted for the relaxation time data. For the specimens exposed to the various humidity conditions used in this program, the shear strength of the moisture exposed specimens was lower than for dry specimens. Shear strengths for the humidity-aged specimens was only about 79% of the dry specimen values (Figure 27). The mechanical property data also revealed however, that for the moisture levels identified in this program, higher moisture levels did not appear to reduce the shear strength of the adhesive any further than the lower moisture level samples. All shear strength values for the environmentally exposed samples appeared to be within one standard deviation. The boiling water test, however, appeared to lower the shear strength to about 57% of its room temperature, dry strength.

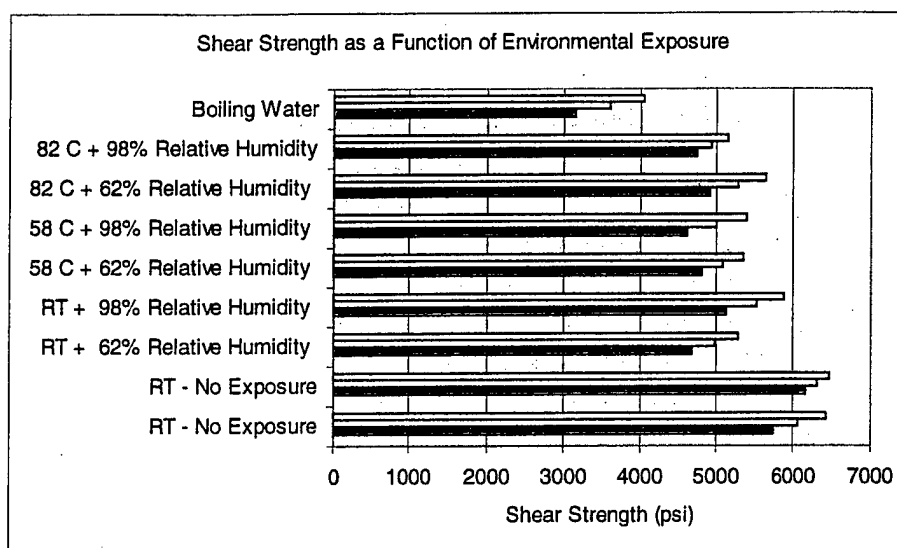


Figure 27. Comparison of ultimate shear strengths as a function of environmental exposure for dry and humidity-aged specimens (bars indicate average values plus and minus one standard deviation)

11.4. Correlation of the Fourier Transform Infrared and Dielectric Relaxation Spectroscopy Data

Upon examination of the DRS and the FTIR data, the following results can be obtained. First of all, because the water molecule itself has a large dipole moment, it should have its own dielectric relaxation process. But the dielectric relaxation spectroscopy technique did not find an isolated relaxation process due to orientation of the water molecule. The DRS technique did however, reveal an increase in the relaxation strength, $\Delta\epsilon$, of moist samples as compared to the dry samples. This apparent increase in the dipole moment is related to the fact that the water molecules interact with the polar group in the adhesive via hydrogen bonding, a fact also noted using FTIR spectroscopy. This data suggests that the water molecule contributes to the β process by cooperative motion with network groups. Additionally, the actual difference in the activation energy between the dry and moist samples was about 20kJ/mol, which corresponds to the bonding energy of the hydrogen bond. This is a very interesting result that suggests that the OH groups of epoxy-amine network relax with the water molecule in a cooperative manner.

11.5 Correlation of the Dielectric Relaxation Spectroscopy Data and the Moisture Content and Double Notch Shear Strengths

The dielectric relaxation times did not correlate with the different moisture levels in the test specimens, at least not at the moisture levels identified in this program (Figure 26). This means that although the water molecules bond to the -OH epoxide groups, the relaxation dynamics do not change with additional -OH/water bonds as originally thought.

Similarly, there doesn't appear to be a correlation between the ultimate shear strength of the adhesive and the different moisture levels identified in this program (Figure 27). It appears that a certain amount of moisture in the specimen does lower the shear strength; however, additional moisture, at least up to the levels identified in this program, results in no additional changes in these properties. Further work would have to be conducted to determine if this is indeed the case.

Because the relaxation times did not correlate with moisture content as expected, dielectric relaxation strengths were then calculated. The purpose of this calculation was to determine if this particular property correlated to moisture content and/or to ultimate shear strength.

Moisture content in the adhesive was determined by weight gain of the double notch shear test specimens in the humidity chamber. The weight gain of the room temperature, dry specimens was 0.0000 grams, the weight gain of the specimens exposed at 60°C and 98% relative humidity was 0.0005 grams, and the weight gain of the specimens exposed to the 24°C, 98% relative humidity specimens was 0.0004 grams.

Relaxation strengths were then determined for the room temperature, dry specimens and the specimens exposed to the 10 day hygrothermal environment of 60°C and 98% relative humidity. From Figure 24, the relaxation strength for the room temperature, dry specimen, tested at room temperature (24°C), was approximately 0.6. For the specimen exposed to the hygrothermal environment of 60°C and 98% relative humidity for 10 days (240 hours), the relaxation strength, tested at room temperature (24°C), was approximately 1.6.

The dielectric relaxation strength was also calculated for five different temperatures for the specimens exposed to the 24°C, 98% relative humidity condition for 720 hours (Figure 28). From this chart, the room temperature, relaxation strength for this condition was determined to be approximately 1.07.

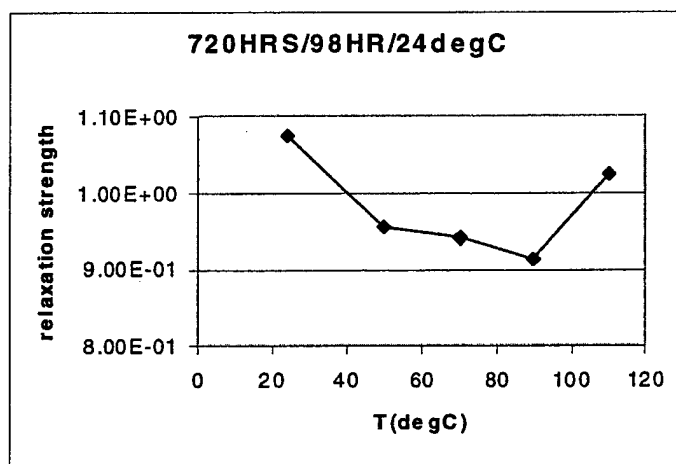


Figure 28. Relaxation strength plotted as a function of test temperature for specimens exposed to 24°C and 98% relative humidity for 720 hours

The ultimate shear strengths of these same specimens were then identified. The ultimate shear strength of the room temperature, dry specimens, tested at room temperature, was determined to be 6319 psi. The room temperature, ultimate shear strength of the specimens exposed to the 60°C, 98% relative humidity condition for 184 hours, was determined to be 5267 psi. (The double notch shear test specimens were only moisture saturated for 184 hours, unlike the dielectric spectroscopy specimens which were exposed for 240 hours. In both cases, however, the specimens were thought to be fully saturated.) The ultimate shear strength of the specimens exposed to the 24°C, 98% relative humidity condition, was determined to be 5502 psi.

A tabular format of the weight gain, the dielectric relaxation strength and the ultimate shear strength for these three specimens is presented in Table 6.

Table 6. Tabular format of correlated data for weight gain (moisture content), dielectric relaxation strength and ultimate shear strength

| Environmental Test Condition | Weight Gain (grams) | Dielectric Relaxation Strength | Ultimate Shear Strength (psi) |
|---|------------------------|-----------------------------------|----------------------------------|
| Room Temperature Dry | 0 | 0.6 | 6319 |
| Room Temperature + 98% Relative Humidity | 0.0004 | 1.07 | 5502 |
| 60C + 98% Relative Humidity | 0.0005 | 1.6 | 5267 |

A plot of the (ultimate shear strength) versus (the dielectric relaxation strength) is shown in Figure 29. In order to determine if the ultimate shear strengths could really be correlated to the dielectric relaxation spectroscopy data, the failure modes of the specimens were determined. The failure mode of the room temperature, dry specimens was cohesive within the adhesive; the failure mode of the specimens exposed to the 60°C and 98% relative humidity was a mainly cohesive with some adhesive failure; and the failure mode of the specimens exposed to the room temperature, 98% relative humidity conditions was also cohesive within the adhesive. This indicates that the failure modes were generally cohesive and the ultimate shear strengths could be correlated to each other and to the DRS data.

The dielectric relaxation strength was then correlated to moisture content in the adhesive. A plot of weight gain versus the dielectric relaxation strength is shown in Figure 30.

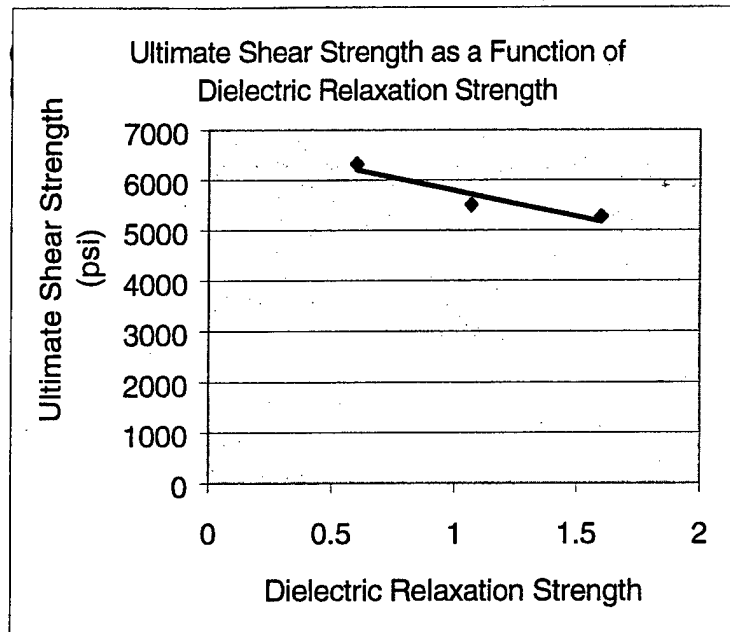


Figure 29. Ultimate shear strength as a function of dielectric relaxation strength for three specimens with different moisture contents

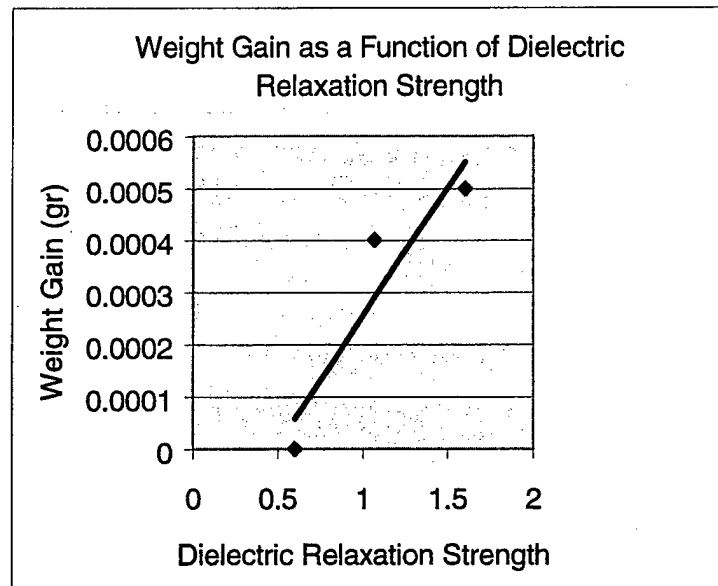


Figure 30. Moisture content as a function of dielectric relaxation strength

In both cases, there were only three data points for correlation of the dielectric relaxation strength versus the ultimate shear strength and moisture content. Because of this, a linear equation was used to correlate the data. Better correlations will be used during the Phase II portion of the program when more data points are available for analysis.

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